

Stabilization of daughter ^{99m}Tc after the β -decay of ^{99}Mo in dihydrido-bis(cyclopentadienyl)molybdenum- (^{99}Mo)

V. MIKULAJ, F. MACÁŠEK, and R. KOPUNEC

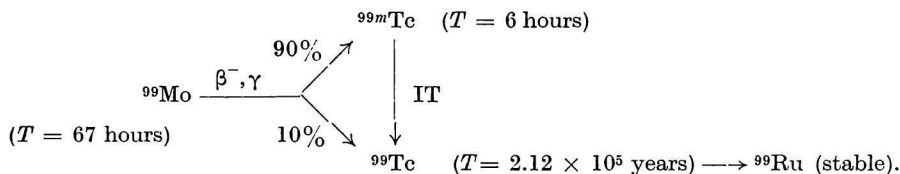
Department of Nuclear Chemistry, Faculty of Natural Sciences, Komenský University, 801 00 Bratislava

Received 13 April 1971

Dedicated to the 70th birthday of Professor M. Dillinger

The chemical forms of the stabilization of daughter ^{99m}Tc after the β -disintegration of ^{99}Mo in dihydrido-bis(cyclopentadienyl)molybdenum- (^{99}Mo) were investigated by radiochemical methods. It was found that ^{99m}Tc is stabilized in high yield in a chemical form which was identified as hydrido-bis(cyclopentadienyl)technetium. The sublimation with temperature gradient and paper chromatography were used for the separation of parent substance from $(\text{C}_5\text{H}_5)_2^{99m}\text{TcH}$. The yield of $(\text{C}_5\text{H}_5)_2^{99m}\text{TcH}$ was determined by sublimation ($88 \pm 2\%$) and paper chromatography ($94 \pm 4\%$) if the daughter ^{99m}Tc was accumulated in the crystals of parent substance. Provided the decay took place in benzene or 3 *N*-HCl, the yield was determined by paper chromatography and extraction ($79 \pm 3\%$).

The radionuclide ^{99}Mo is a parent nuclide of the following genetic chain



It follows from the decay scheme of ^{99}Mo [1] that about 90% of disintegration are withheld on the metastable level of 0.142 MeV corresponding to ^{99m}Tc and about 85% represent a simple β -disintegration with maximum energy of 1.23 MeV. That means that the decay $^{99}\text{Mo} \xrightarrow{\beta^-} ^{99m}\text{Tc}$ may be considered to be practically a "pure" β -decay which is not influenced *e.g.* by the processes of internal conversion.

There are a few papers devoted to the study of the chemical state of daughter ^{99m}Tc after the decay of ^{99}Mo . It was found that ^{99m}Tc occurred predominantly [2] or fully [3] in oxidation degree VII after the decay of ^{99}Mo in molybdenum trioxide. The decay of ^{99}Mo in molybdenum hexacarbonyl was investigated by *Neflodov* and *Toropova* [4] as well as by *Reichold* and *Anders* [5]. *Baumgärtner*, *Fischer*, and *Zahn* [6] utilized the chemical consequences of β -disintegration to the preparation of trace amounts of some compounds containing technetium. These authors found that the daughter technetium is stabilized as a complex cation $[(\text{C}_6\text{H}_6)_2^{99m}\text{Tc}]^+$ in 80–90% yield after the decay of ^{99}Mo bound in dibenzene molybdenum and as $\text{C}_5\text{H}_5^{99m}\text{Tc}(\text{CO})_3$ in a high but not quoted yield provided the decay took place in a $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ molecule [7].

In this study we tried to identify radiochemically the chemical form of the stabilization of ^{99m}Tc after the decay of ^{99}Mo occurring in a molecule of dihydrido-bis(cyclopentadienyl)molybdenum and to estimate the yields of this species.

The formation of the so-called primary molecular ion is an immediate result of the decay of the β -radionuclide constituting a part of molecule. The behaviour of the molecular ion depends on the nuclear characteristics of β -transition, the structure of parent molecule, the chemical properties of daughter element, and other factors [8]. In the case of ^{99}Mo disintegration the recoil energy of daughter atom comes to the fore. The maximum recoil energy of 14.8 eV corresponds to the maximum energy of β -particles of 1.23 MeV. It is obvious that the effect of the recoil energy on the fragmentation of molecular ion cannot be *a priori* neglected.

Experimental

Chemicals and radionuclides used

Molybdenum pentachloride was prepared by chlorinating powdered molybdenum according to the method described in [9].

Dihydrido-bis(cyclopentadienyl)molybdenum was synthesized from molybdenum pentachloride by the reaction with excess sodium cyclopentadienide in the presence of sodium tetrahydridoborate [10]. Tetrahydrofuran was used as solvent. The substance was removed from reaction mixture by sublimation (120°C, 0.01 torr) and the sublimation was repeated at 80°C. A crystalline substance of bright yellow colour was obtained. Melting point 177–178°C (with decomposition, 183–185°C [11]). The substance separated by sublimation was identified by the measurement of mass spectrum [12].

Argon (for welding) and *nitrogen* (for electric bulbs) were purified by allowing them go through a column filled with silica gel on which active copper was deposited (190–210°C) and subsequently through columns with silica gel and molecular sieve Calsit 5.

Benzene, anal. grade, was dried above calcium chloride and distilled.

Diethyl ether, anal. grade, was dried and allowed to go through a column with aluminium oxide (Reanal) and distilled.

Radionuclide ^{99}Mo in chemical form of molybdenum trioxide was used as a starting substance for the syntheses of the labelled compounds of molybdenum. The commercial preparations of specific activity of 20–50 Ci kg^{-1} were used.

Preparation of dihydrido-bis(cyclopentadienyl)molybdenum-(^{99}Mo)

Procedure I

The samples of Cp_2MoH_2 weighing about 80 mg were sealed in an atmosphere of inert gas into quartz ampoules and activated by thermal neutrons in a reactor of the Institute of Nuclear Research of the Czechoslovak Academy of Sciences, Řež near Prague: the density of neutron flux $1 \times 10^{16} \text{ m}^{-2} \text{ s}^{-1}$, activation time 20 hours, dose approximately 10^5 rad. The labelled substance was separated from the activated sample by the sublimation through a layer of glass wool (80°C/0.01 torr). About 20–30% of irradiated sample was sublimed off, the yield of sublimed activity of ^{99}Mo varied within the range from 3 to 5%. A considerable decrease in specific activity and the radiation decomposition caused that the labelled Cp_2MoH_2 was prepared by direct synthesis from labelled compounds of molybdenum.

Procedure II

This procedure was based on the use of the commercial labelled MoO₃ according to the following scheme



The labelled MoO₃ was chlorinated with a saturated solution of chlorine in tetrachloromethane in sealed ampoules at 260–280°C [13]. Subsequently the procedure did not differ from the synthesis of inactive compound. The yields of Cp₂⁹⁹MoH₂ calculated with respect to MoO₃ varied in the range between 25–40%.

Procedure III

The inactive MoCl₅ was irradiated in the reactor under above conditions. The activated MoCl₅ was used directly for the reaction with sodium cyclopentadienide. The specific activity of Cp₂⁹⁹MoH₂ was about 0.4 Ci kg⁻¹. Besides ⁹⁹Mo the radionuclide ³⁵S was also formed by the activation of MoCl₅ by thermal neutrons. But this species did not contaminate the sublimed substance.

The radioactive purity of Cp₂⁹⁹MoH₂ was checked by the measurement of γ-ray spectra and the long-termed measurement of decay curves.

The measurement of activities and yields of daughter ^{99m}Tc

The activities were measured with a scintillation counter containing a “well-type” crystal of NaI(Tl) in connection with a VA-M-120 (VEB Vakutronik, GDR) spectrometer. It was advantageous to measure in the channel corresponding to the region of energies between 0.14–0.18 MeV.

For the measurement of the yields of daughter ^{99m}Tc isolated by a certain separation method the samples in which ^{99m}Tc was in radioactive equilibrium with the parent ⁹⁹Mo were analyzed. Provided the daughter ^{99m}Tc with counting rate n_1 was isolated from a sample with counting rate n , then its yield was calculated according to the formula.

$$x_1 = \frac{n_1}{k n} \cdot 100\%, \quad (1)$$

where x_1 is the yield of ^{99m}Tc and k is an empirical coefficient the value of which depends on the decay scheme of ⁹⁹Mo and the method of activity measurement. Under the conditions used it was $k = 0.89$ (measurement in channel) or $k = 0.82$ (integral measurement). Provided the isolated fraction contained a certain amount of ⁹⁹Mo, a correction was made and the yield was calculated according to the formula

$$x_1 = \frac{n_1 - x_2(1 - k) n}{k n} \cdot 100\%, \quad (2)$$

where x_2 is the fraction of ⁹⁹Mo. This fraction was estimated by repeated measurements of the counting rate of samples after the total decay of original ^{99m}Tc (60–70 hours).

Experimental methods

The labelled Cp₂MoH₂ was kept in an argon or nitrogen atmosphere in the Schlenk test tubes sealed with paraffin wax at room temperature and in the dark. It was either

in crystalline state or dissolved in a convenient solvent. After the radioactive equilibrium had been established (60–70 hours), the chemical properties of the daughter ^{99m}Tc were investigated. It was the sublimation method, paper chromatography, electrophoresis and extraction which were used for this purpose. Because of the oxidability of the parent substance all operations were carried out in an inert atmosphere. The solvents were deprived of oxygen by a thorough bubbling through with an inert gas.

In the first series of experiments ^{99}Mo decayed in the crystals of parent substance. Individual samples were directly sublimed or dissolved in a convenient solvent and analyzed. In the second series of experiments the parent substance was dissolved and the daughter ^{99m}Tc was thus formed in solution. This solution was analyzed by the above-mentioned method after the radioactive equilibrium had been established. The investigated solutions were transparent of bright yellow colour. They oxidized in air and their colour changed into intense dark brown. The concentrations of $\text{Cp}_2^{99}\text{MoH}_2$ varied in the range from 10^{-2} to 10^{-1} mol l^{-1} .

Sublimation with temperature gradient

This procedure was used to obtain information about the volatility of daughter technetium. The device used (Fig. 1) consisted of a glass tube with internal diameter of 6 mm and 40 cm length which had two ground glass joints at the end. By means of one of these ground glass joints the tube could be connected to a pump whereas the second one allowed to put the ampoule with a sample into the tube. After putting the sample into the tube a pad of glass wool was inserted and the tube was filled up with small glass balls. To produce a temperature gradient a glass oven was used. The diameter of this oven was a little greater than that of sublimation tube. The temperature gradient used for sublimation is shown in Fig. 1. The sublimation was carried out at the pressure of 0.01 torr. The sublimation finished, the distribution of activity was measured along the tube by two centimeters with a scintillation head shielded with a convenient lead covering. After a certain period of time, the measurements were repeated and the distribution of technetium was appreciated according to the decrease and increase of the activity in particular zones.

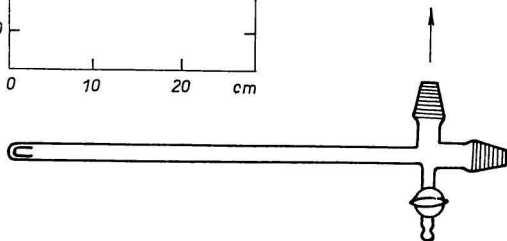
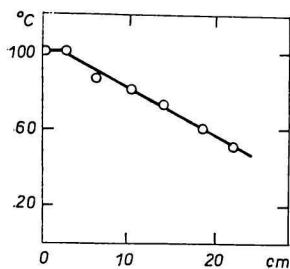


Fig. 1. Sublimation tube with temperature gradient. The oven is not pictured.

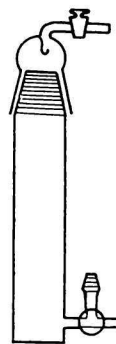


Fig. 2. Chromatographic chamber for the work in an inert atmosphere.

Paper chromatography

This method was applied in the form of ascending chromatography. The sample application and development were carried out in an inert atmosphere. The working procedure was as follows. The paper strip was hung in the chromatographic chamber (Fig. 2), air was sucked off with an oil pump, inert gas was let in through a three-way cock and the chamber was washed for about 30 minutes. Through the three-way cock the sample of solution (about 10 μ l) was applied on the paper with a micropipette. Then the chamber was once more washed with an inert gas for a few minutes, the elution solution deprived of oxygen was added and the chamber was closed. After the development, the paper was cut into the strips of 1 cm width the activities of which were measured in a "well-type" crystal. The position of Cp₂MoH₂ was fixed easily even by sight, for the sample oxidized in air, and a dark brown spot appeared on paper. Whatman No. 3 paper impregnated with paraffin oil was used while a mixture of methanol with water (5 : 1 volume) was applied as eluent. Benzene, cyclohexane, and *n*-hexane were also used as eluents, but in these cases the paper was not impregnated.

Electrophoresis

The device used enabled us to apply the sample and to perform the electrophoresis in an atmosphere of inert gas. Whatman No. 3 paper was employed as a carrier. The measurements were carried out by using the working voltage of 400 V (20 V cm⁻¹), platinum wire electrodes and 0.015 *N*-HCl solution as an electrolyte solution. The substance was applied in dissolved state (3 *N*-HCl solution). The activities were measured in an analogous way as in paper chromatography.

Results and discussion*Identification of the main chemical form of ^{99m}Tc stabilization*

The parent substance denoted ⁹⁹Mo Cp₂MoH₂ was prepared in three different ways. On account of practical reasons (non-reduced specific activity, one-step synthesis) procedure III was preferred. It is worth noticing that the results did not depend on the method of preparation of parent substance.

After the accumulation of daughter technetium in the crystals of parent substance, the individual samples were sublimed. The distribution of activity along the sublimation tube is shown in Fig. 3. It is obvious that the prevailing part of daughter ^{99m}Tc is more volatile than the parent substance and is, therefore, deposited at the outlet of oven at the temperatures between 40–50°C. A smaller part is non-volatile.

When the parent substance was dissolved in 3 *N*-HCl and the solution subjected to electrophoresis, it appeared that the daughter ^{99m}Tc as well as the parent substance migrated to cathode in acid solutions (Fig. 4). This effect indicated that both substances were present as complex cations. Provided the parent substance was dissolved in benzene and the solution was applied to paper chromatography, it was found that both Cp₂⁹⁹MoH₂ and ^{99m}Tc moved practically with the front of solvent (Fig. 5) on condition that such eluents as benzene, cyclohexane, and *n*-hexane were used. Only a small part of the daughter ^{99m}Tc remained at the starting line.

At last, Cp₂⁹⁹MoH₂ was dissolved in 3 *N*-HCl and the daughter technetium was accumulated in solution. After benzene extraction practically no activity passed into the organic

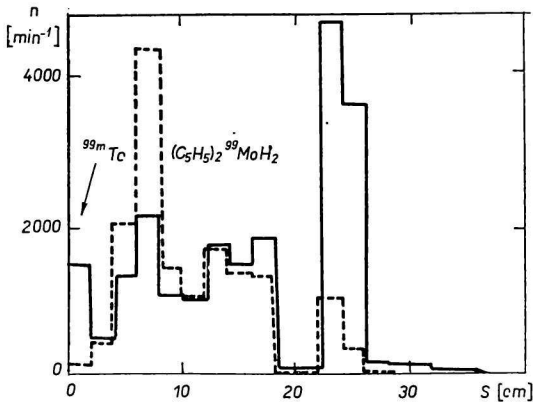


Fig. 3. Gradient sublimation of $(C_5H_5)_2^{99}MoH_2$.

Distribution of activity along the sublimation tube:
 — immediately after sublimation;
 - - - 36 hours after sublimation.

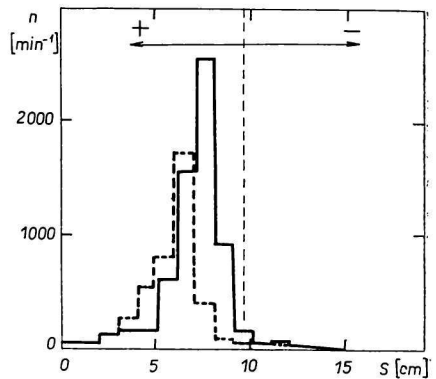


Fig. 4. Electrophoresis of $(C_5H_5)_2^{99}MoH_2$. Parent substance dissolved in 3 N-HCl.

Distribution of activity:
 — immediately after electrophoresis;
 - - - 48 hours after electrophoresis.

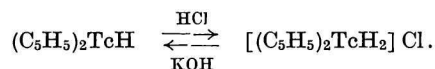
phase. Only after additional alkalization of aqueous phase with potassium hydroxide the daughter technetium as well as $Cp_2^{99}MoH_2$ was extracted into benzene.

From the results of these experiments it follows that the daughter ^{99m}Tc is predominantly stabilized in a chemical form which is characterized by the following properties:

- it is volatile and sublimates easier than the parent substance $Cp_2^{99}MoH_2$;
- its chromatographic properties are similar to the properties of parent substance, it moves with the front of solvent even if nonpolar eluents such as benzene, cyclohexane, and *n*-hexane are used;
- it occurs as a cation in acid aqueous solutions and is not extracted with benzene;
- it is extracted with benzene from alkaline aqueous solutions.

On the basis of these properties of the daughter ^{99m}Tc as well as on the assumption that the stabilization of primary molecular ion is effective provided its structure corresponds to a stable compound of daughter element we came to the conclusion that the prevailing portion of ^{99m}Tc is stabilized in the form of hydrido-bis(cyclopentadienyl)-technetium $(C_5H_5)_2^{99m}TcH$ or of corresponding cation $[(C_5H_5)_2^{99m}TcH_2]^+$.

The following hydrides of cyclopentadienyl compounds containing transition elements have hitherto been synthesized: Cp_2TaH_3 [11], Cp_2MoH_2 [11, 14], Cp_2WH_2 [11], Cp_2TcH [15], and Cp_2ReH [16, 17]. All these compounds except for those including tantalum exhibit the properties of bases and are insoluble in water. But they are soluble in organic solvents as well as in acid aqueous solutions under formation of complex cations, *e.g.*



Hydrido-bis(cyclopentadienyl)technetium was synthesized in weighable amounts by Fischer and Schmidt [15] in an analogous way as other hydrides by using the reaction of sodium cyclopentadienide with technetium(IV) chloride in the presence of $NaBH_4$.

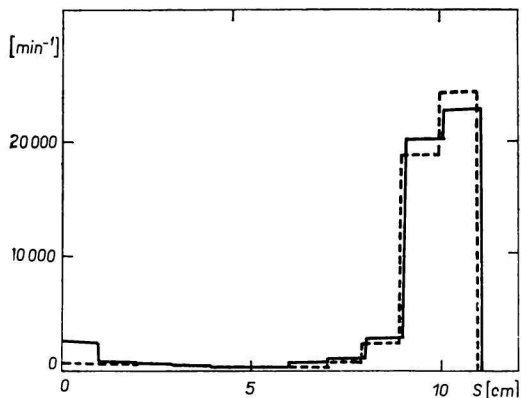


Fig. 5. Paper chromatography of $(C_5H_5)_2^{99}MoH_2$. Developing solvent: benzene.

Distribution of activity:

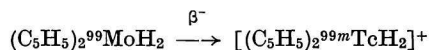
———— immediately after development; - - - - - 11 hours after development.

The substance forms yellow crystals which sublime at 40–60°C and 0.01 torr, are soluble in benzene, toluene, and to a lesser extent in hexane. These properties conform with the properties of the main chemical form of stabilized daughter ^{99m}Tc which were found by radiochemical methods.

β-Decay of $Cp_2^{99}MoH_2$ in crystals and in solution

On the basis of the results involving the fact that the homogeneity of the main fraction of daughter ^{99m}Tc as well as its principal chemical properties were demonstrated, it was possible to determine the yield of $Cp_2^{99m}TcH$ or $[Cp_2^{99m}TcH_2]^+$. The yields were estimated by gradient sublimation, paper chromatography, and extraction. In the case of sublimation the portion of non-sublimed (non-volatile) ^{99m}Tc was calculated with respect to the total amount of daughter ^{99m}Tc and the yield of $Cp_2^{99m}TcH$ was determined as a complement to 100%. Provided the paper chromatography on impregnated paper was used, the chromatograms had the character shown in Figs. 6 and 7. Under these conditions, the values of R_F factor of parent substance and $Cp_2^{99m}TcH$ were 0.75 and 0.60, respectively. A certain part of the activity corresponding to the daughter ^{99m}Tc remained on the starting line or exhibited the R_F value of 0.3. These two forms of ^{99m}Tc were not identified chemically and either of them can be considered for an “inorganic” form of ^{99m}Tc identical with the non-volatile form. The results of the determination of yields are presented in Table 1. The errors of yield estimation were calculated from the scattering of the values obtained, the probability limit being 0.90. The agreement between the yields obtained by different methods is satisfactory. Provided the daughter ^{99m}Tc arose in solution, the change in the concentration of parent substance in the concentration range between 0.01–0.1 M had no effect on the yield of $Cp_2^{99m}TcH$. The substitution of benzene for diethyl ether did not change the character of chromatogram either.

The high yield of $Cp_2^{99m}Tc$ is in agreement with the theoretical idea that the primary molecular ion formed after the β-decay of ^{99m}Mo



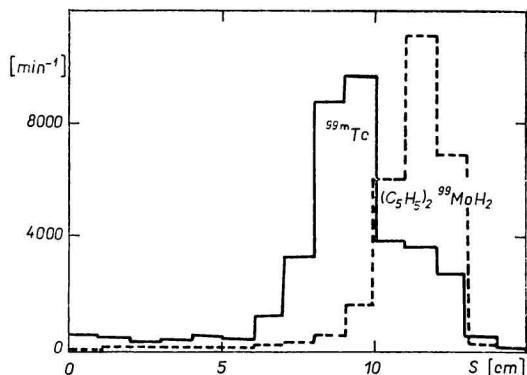


Fig. 6. Paper chromatography of $(\text{C}_5\text{H}_5)_2^{99\text{m}}\text{MoH}_2$. Developing solvent: methanol—water (5 : 1).
Distribution of activity:

————— immediately after development; 30 hours after development.

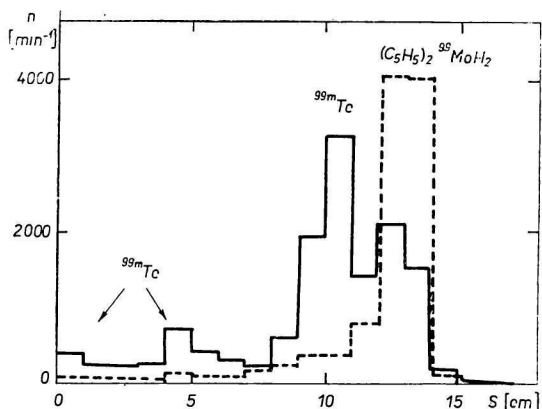


Fig. 7. Paper chromatography of $(\text{C}_5\text{H}_5)_2^{99\text{m}}\text{MoH}_2$ in benzene solution. Developing solvent: methanol—water (5 : 1).
Distribution of activity:

————— immediately after development; 18 hours after development.

is isoelectronic with respect to the parent molecule and corresponds to the stable cation of dihydrido-bis(cyclopentadienyl)technetium(III). The results indicate that such stable formation may remain in the matrix of the crystal lattice of parent substance and a splitting of proton may take place at increased temperature or after the dissolution of substance.

The fragmentation of molecular ion may also be affected by the recoil energy of daughter atom or by the electron "shake" due to the change in nuclear charge during β -decay [8]. The effect of these factors or secondary reactions is in no way very significant what is evidence of a considerable stability of the bis-cyclopentadienyl compounds of transition elements.

Table 1

Yields of $(C_5H_5)_2^{99m}TcH$ after the β -decay of ⁹⁹Mo
in dihydrido-bis(cyclopentadienyl)molybdenum-(⁹⁹Mo)

Decay	Method of estimation	Experiments	Yield $(C_5H_5)_2^{99m}TcH$ [%]
In crystals	Sublimation	5	88 ± 2
In crystals	Paper chromatography	3	94 ± 4
In benzene solution	Paper chromatography	5	79 ± 3
In 3 N-HCl	Benzene extraction*	1	78

* After alkalization of aqueous phase (3 N-KOH).

References

- Way, K., Artna, A., Fuller, G., Gove, N. B., Nakasima, R., and Lieshout, R., *Nuclear Data Sheets*, Set 3, National Research Council, National Academy of Sciences, Washington, 1961.
- Münze, R., *Kernenergie* **4**, 808 (1961).
- Ferradini, C., Carlier, R., Genet, M., and Pucheault, J., *Radiochim. Acta* **12**, 1 (1969).
- Nefiodov, V. D. and Toropova, M. A., *Zh. Neorg. Khim.* **3**, 231 (1958).
- Reichold, P. and Anders, H. P., *Radiochim. Acta* **5**, 44 (1966).
- Baumgärtner, F., Fischer, E. O., and Zahn, U., *Chem. Ber.* **94**, 2198 (1961).
- Baumgärtner, F., Fischer, E. O., and Zahn, U., *Naturwissenschaften* **49**, 156 (1962).
- Nefiodov, V. D., Zaitsev, V. M., and Toropova, M. A., *Usp. Khim.* **32**, 1367 (1963).
- Handbuch der präparativen anorganischen Chemie*. (G. Brauer, Editor.) P. 644. (Russian translation.) Moscow, 1956.
- King, R. B., *Organometallic Syntheses*, Vol. I, p. 79. Academic Press, New York, 1965.
- Green, M. L. H., McCleverty, J. A., Pratt, L., and Wilkinson, G., *J. Chem. Soc.* **1961**, 4854.
- Macášek, F., Mikulaj, V., and Drienovský, P., *Collect. Czech. Chem. Commun.* **35**, 993 (1970).
- Michael, A. and Murphy, A., *Amer. Chem. Soc. J.* **44**, 380 (1910).
- Fischer, E. O. and Hristidu, Y., *Z. Naturforsch.* **15b**, 135 (1960).
- Fischer, E. O. and Schmidt, M. W., *Angew. Chem.* **79**, 99 (1967).
- Green, M. L. H., Pratt, L., and Wilkinson, G., *J. Chem. Soc.* **1958**, 3916.
- Wilkinson, G. and Birmingham, J. M., *J. Amer. Chem. Soc.* **83**, 4474 (1961).

Translated by R. Domanský

11
112
112